Appendix M. Chemical Analytical Method
Chloropicrin - sorbent tubes
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Revised:

Determination of Chloropicrin Desorbed from XAD-4 Resin Tubes

Scope: This method describes the desorption and determination of chloropicrin from XAD-4 air sample tubes.

Principle: Chloropicrin in the air that has been adsorbed onto XAD-4 resin is desorbed from the resin with hexane. Subsequently, chloropicrin is quantified using a gas chromatograph with an Electron Capture Detector (ECD).

Reagents, Equipment and Instrument:

Reagents:

1. Hexane, pesticide residue grade
2. Chloropicrin, CAS# 76-06-2, 1.0 mg/mL in hexane, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
3. XAD-4 resin, obtained from Rohm and Hass, cleaned up in the laboratory with acetone and hexane (see SOP # 103.0).

Equipment:

1. Test tubes, 50 mL, with Teflon-liner caps
2. Pasture pipettes and micro-syringes
3. Volumetric flasks, various size
4. Sampling tube
5. Thermolyne Vortex Maxi Mixer II
6. Volumetric pipettes, various size
7. Funnel, short stem and large exit diameter fits into the extraction test tube
8. Airchek Sampler, Model 224-PCXR7, with a flow about 1-2 L/minute for trapping efficiency use.
9. Autosampler vial, 2 mL

Instrument:

Hewlett Packard model 5890 gas chromatograph with autosampler and an electron capture detector.

Analysis:

Sample Extraction:

1. Remove samples from freezer. Allow samples at room temperature for 20-30 minutes before extraction.
2. Place a funnel in the sample extraction tube, Remove the top glass wool from the XAD-4 sampling tube using a Pasture pipette. Push the glass wool down into the extraction tube. Pour the resin into the extraction tube via a funnel. Tap the side of sampling tube to allow adhered resin beads to drop into the extraction tube. Using the pipette, push the bottom glass wool and metal screen into the extraction tube.
3. Pipette a known volume of hexane and wash the inside wall of the sampling tube into the extraction tube. A volume of 10 mL solvent for tube containing 10 mL XAD-4 resin is suggested.
4. Extract chloropicrin from XAD-4 by mixing for 60 seconds on a vortex mixer.
5. Allow the mixture at room temperature for 1-2 minutes. Transfer about 1 mL extract from the bottom of the tube into an autosampler vial and cap it tightly. Store extract in a second autosampler vial is recommended.
6. Determine chloropicrin using a gas chromatograph with electron capture detector.

Instrument Conditions:

Electron Capture Detector:
Hewlett Packard 5890 GC with ECD

Column:	DB-5MS (5% phenyl-methyl polysiloxane) 30 m x 0.25 mm x 1.0μm
Carrier gas:	Helium: column head pressure: 10.5 psi, flow rate: 0.63 mL/minute
Detector gas:	Nitrogen: flow rate: 60 mL/minute
Injector:	200 °C splitless
Detector:	ECD set temperature at 350 °C
Septum purge:	2 mL / minute
Temperature Program:	Initial Temp: 40 °C hold for 5 minutes
	Rate A: 10 °C / minute to 140 °C
	Rate B: 30 °C / minute to 210 °C hold for 1 minute
Injection volume:	2 μL by autosampler
Retention time:	12.8 ± 0.1 minute

Calculations:

Results are generally calculated by Hewlett Packard ChemStation software using its piecewise curve-fitting option to account for differences in peak height response. Alternatively, results are calculated manually using the formula below:

$$\mu g\ \textbf{Chloropicrin} = \frac{(\text{peak ht sample})\ (\eta g \text{ std injected})\ (\text{sample final volume, mL})}{(\text{peak ht standard})\ (\mu L \text{ injected})}$$

Method Performance:

Quality Control:

1. A seven-point calibration curve of 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 ηg/μL chloropicrin was obtained at beginning and the end of each set of samples.
2. Each sample is analyzed two times to insure reliability of the chromatography. If the signal of the sample is greater than that of the highest concentration of the calibration curve, the sample is diluted to within the calibration range and reanalyzed.

Method Detection Limit:

Method Detection Limit (MDL) refers to the lowest concentration of analytes that a method can detect reliably in either a sample or blank. To determine the MDL, 7 sample tubes are spiked individually with 0.2 μg of chloropicrin. These spiked samples along with a blank are analyzed using the described method. The MDL is calculated using the following equation:

$$MDL = tS$$

where;

- **t** is the Student 't' value for the 99% confidence level with n - 1 degrees of freedom (n - 1, 1 - α = 0.99).
- **n** represents the number of replicates.
- **S** denotes the standard deviation obtained from replicate analyses

Spike	μg Spiked	μg Recovered
1	0.2	0.156
2	0.2	0.161
3	0.2	0.159
4	0.2	0.166
5	0.2	0.164
6	0.2	0.167
7	0.2	0.172

Average μg Recovered = 0.164
Standard Deviation = 0.005
The calculated MDL for chloropicrin is 0.016 μg.

Reporting Limit:

Reporting Limit refers to the level above which quantitative results may be obtained. In this method the reporting limit is rounded to 0.2 μg per resin tube .

Validation:

Resin tubes are spiked at three different levels of chloropicrin, 1, 10 and 100 μg. Spiked samples are extracted with hexane. The 10 μg and 100 μg samples are diluted accordingly. The amount of chloropicrin in the extract is subsequently determined.

Validation: continued:

Recoveries of chloropicrin are as shown below:

Spike Level (µg/sample)	Result (µg/sample)	Recovery (%)
1.0	0.757	75.7
	0.82	82
	0.83	83
	0.893	89.3
	0.864	86.4
10.0	8.74	87.4
	7.8	78
	7.56	75.6
	8.62	86.2
	8.39	83.9
100	88.9	88.9
	77	77
	74	74
	91.2	91.2
	88.7	88.7

Discussion:

1. Injector port temperature should be set at 200°C. It is noticed that when injector temperature set at 240°C, chloropicrin converts to the dimer (hexachloroethane) completely.
2. For a better sensitivity, one should use EC detector. However, MSD SIM mode is a good tool for confirmation. Confirmation to the level 0.5 µg chloropicrin per sample has been achieved.

References:

1. *NIOSH Manual of Analytical Methods, Second Edition Method S212, S104, 260.* Available from Superintendent of Documents, US. Government Printing Office, Washington, DC, 20402
2. Guide to Chemicals used in Crop Production, Information Canada, P. 118, 1973
3. Scott Fredrickson, CDFA, *The analysis of air samples for chloropicrin,* Center for Analytical Chemistry, Worker and Health Safety, February 2, 1982.
4. James Seiber, Final Report to the Air Resources Board Pilot Analysis of Chloropicrin in Air, Contract #A5-169-43. Dated October 28,1987.
5. J&W Scientific Catalog and Reference Guide 1994-95, P.159.

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